

LD-JC: Laser Desorption Jet-Cooling Spectroscopy.

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ABSTRACT

Laser desorption followed by jet-cooling allows wavelength-selective as well as mass-selective detection of organic molecules desorbed from a surface without fragmentation. The absolute detection sensitivity is demonstrated with the perylene molecule. A two-color REMPI spectrum (400 wavelength points) of perylene is recorded using only 30 picogram of material. Rotational cooling to 5-10 K is demonstrated with laser-desorbed anthracene; vibrational cooling below 15 K is demonstrated with laser-desorbed diphenylamine. The ability to take a "snapshot" of molecules on a surface is illustrated with the spectrum of benzoic acid monomers. Other applications are discussed, i.e. PABA dimer spectroscopy and detection of C_{60} .

1. INTRODUCTION

The novel technique of laser desorption jet cooling spectroscopy (LD-JC), which will be discussed here, is especially important in two areas: spectroscopy of very low vapor pressure complex molecules, and organic surface analysis. (a) Spectroscopy of complex organic molecules is a challenge because the large number of internal degrees of freedom causes a hopelessly congested spectrum at all but the lowest temperatures. On the other hand densities in the gas phase are prohibitively low at all but the highest temperatures. Furthermore, most of the larger molecules fragment at elevated temperatures. (b) Detection and identification of organic molecules on surfaces is a very general analytical problem with ever increasing technological applications. In the electronics industry, for example, ever smaller amounts of surface contaminations are becoming important. Other examples include the study of biological materials, certain pharmaceuticals, geophysical samples, or small organic particles. Whereas volatile samples can be analyzed by the powerful combination of gas chromatography and many mass-spectrometric techniques, solid compounds generally need an initial step of solution or vaporization, which may alter the compounds to be studied. Indeed most routine surface analytical techniques involve heating or exposure to electrons or ions, conditions under which most organic molecules are not stable.

Both the areas of organic spectroscopy and surface analysis are served with an approach in which fragile molecules can be vaporized without fragmentation, and subsequently cooled and studied with both optical (UV-vis) and mass spectrometry. Laser desorption can provide heating to the order of 1000 K in 10 ns. Thus the timescale for heating can be made shorter than that for vibrational excitation of the bond that would lead to fragmentation¹. This idea was discussed by Hall² in terms of desorption *vs* reaction probabilities. If the activation energy and the pre-exponential factor are larger for desorption than for reaction on the surface, then desorption will be preferred over reaction at high heating rates. Another way of describing this is by assuming that the laser energy is absorbed by the substrate, rather than by the molecule and that the bond to the surface acts as a bottleneck for the flow of energy into the molecule³. It has been shown experimentally that molecules can be desorbed intact and with relatively little internal energy at high heating rates, while they decompose at low heating rates.⁴

In the laser desorption jet-cooling technique, molecules originally adsorbed on a surface are desorbed with a laser pulse close to the orifice of a pulsed jet expansion. The laser-desorbed molecules are entrained in the jet and their internal energy is cooled by multiple collisions in the expansion region. In the collision-free region of the expansion the molecular beam is probed with one or more ionization laser(s), and ions are mass- and wavelength-selectively detected⁵⁻¹⁰. Cooling is important both for simplifying the spectroscopy of the desorbed molecules¹¹ and for increasing the detection efficiency; one can take advantage of resonance-enhanced multi-photon ionization (REMPI) spectroscopy to achieve sensitive and selective detection¹². Even when non-resonant ionization techniques are used to detect the entrained molecules, cooling has the advantage that it results in less fragmentation following ionization.

$P_o = 1/N_o$ is molecule-dependent, but can be written as a product of the ionization efficiency P_i and the apparatus efficiency P_{ops} . The latter measures the probability with which the laser-desorbed molecules are brought into interaction with the detection laser(s), and is molecule-independent.

Laser desorbed, jet-cooled perylene was resonantly excited to the S_1 state with $10 \mu\text{J}/\text{mm}^2$ of 416-400 nm radiation. Even at the highest ionization laser powers used, no fragmentation of the perylene was seen when the wavelength for ionization was chosen at 311.5 nm, which just barely exceeds the ionization limit of 6.97 eV. Several measurements were performed to obtain reliable numbers for the overall detection efficiency of laser-desorbed jet-cooled perylene. We find that (5 ± 1) perylene-ions can be detected for every 10^6 perylene molecules originally in the desorption laser spot.

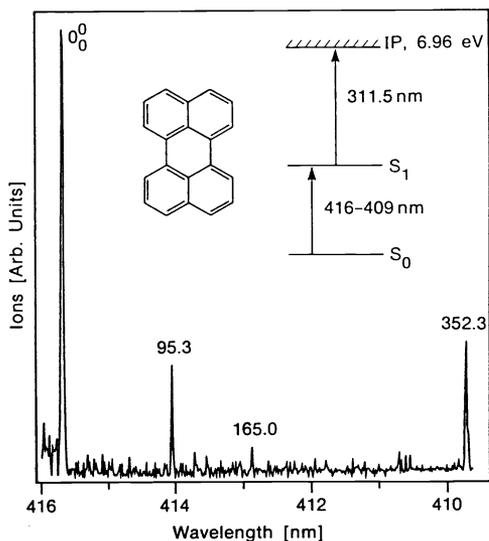


Figure 2: LD-JC/REMPI spectrum, obtained from 30 picogram of perylene.

To demonstrate this sensitivity of the laser desorption jet-cooling technique a two-color (1 + 1) REMPI spectrum of perylene using less than 30 picogram of material was recorded. For this a sample with a 5 Å perylene layer on top of a 600 Å coronene layer and covered with another 2000 Å coronene layer was used. The resulting spectrum of perylene is shown in Figure 2. It is important to note that the perylene spectrum was recorded without interference of the coronene, present in the beam in much larger amount. Ions were detected on the perylene mass while the resonant excitation laser was scanned over part of the $S_1 \leftarrow S_0$ transition. The spectrum consists of 400 wavelength steps (0.16 Å each), and the signal was averaged over 6 shots at each wavelength setting. Apart from a strong origin, two weaker vibrations at 95.3 cm^{-1} and at 165.0 cm^{-1} together with a strong vibration at 352.3 cm^{-1} are recognized. The spectrum is identical to the LIF spectrum of perylene¹⁵. As a low laser power was used for the resonant step, no overtones from the weaker vibrations are seen. The 352.3 cm^{-1} vibration should appear just as strong as the electronic origin. The difference in intensity indicates that the sample was partly depleted during the laser scan. From the thickness of the perylene layer together with the area of the desorption spot of $(4.3 \pm 0.2) \times 10^{-4} \text{ cm}^2$, we deduce that we started with 30 picogram of perylene in the desorption laser spot.

At the end of the scan there is still some material left, and probably only 20 picogram was used. *This means that on average 8.5 femtograms of perylene (33 attomoles) were desorbed per laser shot.*

In a separate experiment we measured the ionization efficiency of perylene for REMPI conditions identical to the ones used here. This efficiency, P_i , was found to be 25%. This means that we find the detection sensitivity for a given molecule as 2×10^{-5} times the ionization efficiency of that specific molecule. The apparatus efficiency $P_{ops} = 2 \times 10^{-5}$ consists of two factors: first, the fraction of laser-desorbed molecules which passes through the skimmer, and second, the fraction of molecules passed that interact with the detection laser. The first fraction is of the order of 0.1%, while the second fraction is typically of the order of 1%.

It should be noted that such a high ionization efficiency requires effective cooling, in order to ensure optimum population of the lowest vibrational state, as well as a narrow rotational line profile. Furthermore, if one wants to put these numbers in a general perspective, it should be pointed out that there exists a general problem with REMPI detection. Very often efficient *and* selective ionization is not possible simultaneously for molecules that need a higher frequency photon to be ionized from the intermediate state than the photon used for resonant excitation. The density of states above the first electronically excited state is often so high that most ions are produced by the ionization laser alone, by efficient two-photon ionization via this quasi-continuum, without any effect of the resonant excitation laser. Of course, one can reduce the intensity of the ionization laser to suppress the single color

In the following sections the technique will be described, the sensitivity and the cooling characteristics will be demonstrated, and applications will be discussed.

2. APPARATUS

A schematic of the experiment is shown in Figure 1. The sample is mounted in front of a pulsed valve (General Valve) with a 0.5 mm nozzle diameter. The sample bar is positioned within 0.1 mm of the nozzle plate. The level of the sample can be varied continuously, and typically the sample is 0.5-2.0 mm below the molecular beam axis. The desorption laser hits the sample from above, and the position of the desorption laser spot relative to the nozzle can be adjusted. Positioning the spot 0.5-1.0 mm in front of the nozzle turns out to be best for optimum cooling. A KrF (248 nm) excimer laser with unstable resonator optics is used for desorption. The beam is attenuated to 50 - 100 μJ . and loosely focused into a spot of less than 0.25 mm diameter on the sample.

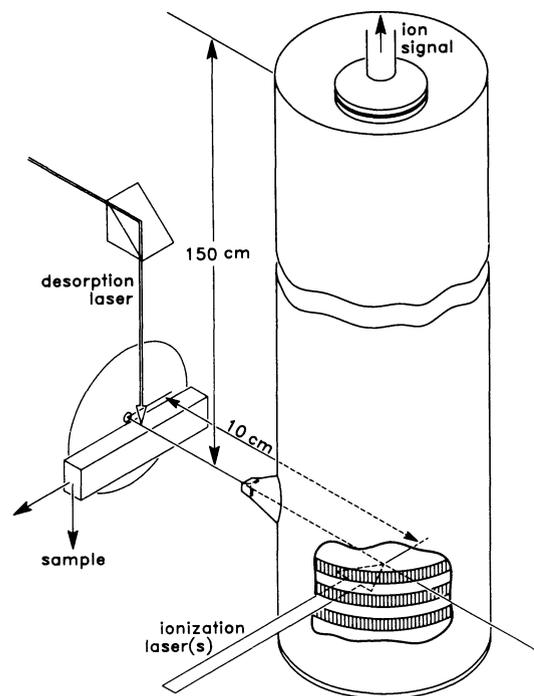


Figure 1: LD-JC apparatus

In all experiments described below, Ar, with a backing pressure of 8 atm., is used as the drive gas. Several types of sample holders are used, depending primarily on the vapor pressure of the molecules under study. When material is desorbed from a porous matrix the desorption laser power can be adjusted to completely remove the surface layer with each shot. The layer is replenished between desorption shots by diffusion from the bulk, and a more stable signal is obtained. This works especially well for molecules with a higher vapor pressure, which are more mobile in the matrix.

Following desorption, the desorbed molecules are entrained in the jet and their internal degrees of freedom are cooled by multiple collisions with the drive gas. A fraction of the entrained molecules passes through the 1x4 mm slit skimmer, 2.4 cm away from the nozzle. The beam enters the differentially pumped detection chamber, cooled to liquid nitrogen temperature, and is intersected, 9.4 cm away from the nozzle, by ionization laser(s). Ions are formed between the extraction plates of a Wiley-McLaren-type ¹³ linear time-of-flight mass spectrometer. The ions pass through a 150 cm long, grounded drift tube and are collected on a 2" dual channel plate. The signal from the channel plates is amplified and recorded on a digital oscilloscope. The mass spectra are processed by an IBM PC. Under typical operating conditions, unit mass resolution up to 300 amu is obtained.

For resonant excitation of the jet-cooled organic molecules, the frequency-doubled output of a Quanta Ray or Lumonics dye laser pumped by the second and third harmonic, respectively, of a single Nd:YAG laser are used. For the ionization process either the same or the second dye-laser, an excimer laser, or the third harmonic of the Nd:YAG are used. An excimer laser, operating on KrF (248 nm), ArI⁺ (193 nm), or F₂ (157 nm), is also used for non-selective ionization of laser-desorbed species. All experiments are performed with unfocused ionization beams. The laser fluence applied for resonant excitation in the various organic molecules is on the order of 1-10 $\mu\text{J}/\text{mm}^2$. For ionization out of the intermediate state laser fluences of 0.1-1.0 mJ/mm^2 are used.

3. DETECTION SENSITIVITY

The overall detection sensitivity of laser desorption jet-cooling is one of the important characteristics to be determined ¹⁴. One wants to know the minimum number of molecules, N_0 , needed within the desorption laser spot on the surface in order to yield a detectable, mass- and wavelength-selected ion signal. The overall detection sensitivity

process relative to the resonant two-color (1 + 1)-REMPI process, but this reduces also the overall ionization efficiency.

4. COOLING CHARACTERISTICS

4.1 Rotational Cooling

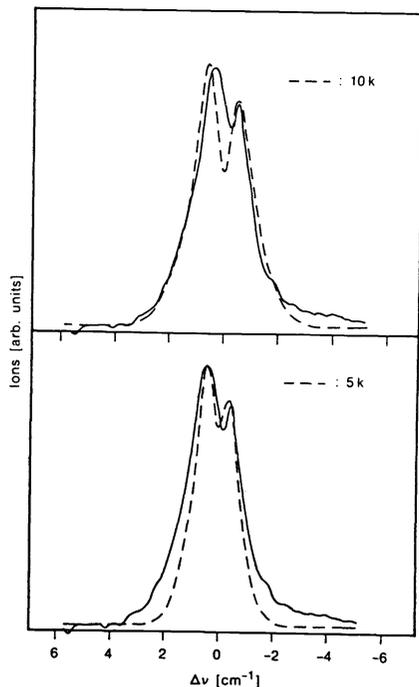


Figure 3: Rotational contours of anthracene $S_1 \leftarrow S_0$ transition.

To determine the degree of rotational cooling, the rotational envelope of the origin of the $S_1 \leftarrow S_0$ electronic transition of laser-desorbed anthracene was measured. The jet-cooled anthracene was pumped into its first electronically excited singlet state with a laser fluence of about $2 \mu\text{J}/\text{mm}^2$ to avoid saturation of the resonant step. Ionization out of the S_1 state was performed with 307 nm radiation from another dye laser, thus reaching slightly above the ionization potential of 7.44 eV¹⁶. Ions were detected on the parent mass (178 amu). In Figure 3 the measured rotational contour of the $S_1 \leftarrow S_0$ transition of anthracene (solid curve) is shown. The excitation laser was scanned in 0.030 Å steps over the electronic origin at 361.1 nm. The ion signal at each wavelength position was averaged over 100 shots. The measured rotational contour is compared with the simulated rotational contour for a rotational temperature of 10 K (upper panel) and 5 K (lower panel). Simulated curves are taken from the work by Amirav et al.¹⁷ and include a 0.5 cm^{-1} linewidth for the excitation laser, which is the same as the linewidth of our doubled dye laser. As explicitly noted in the work of Amirav et al.¹⁷, there are three features in the rotational contour that are sensitive to the rotational temperature. Two of these, the frequency splitting between the $\Delta K = +1$ and the $\Delta K = -1$ branches and the depth of the minimum between them, are fitted best with the 5 K simulation. The third one, the overall width of the rotational contour, agrees best with the 10 K simulation. We conclude therefore that the rotational temperature of the laser-desorbed jet-cooled anthracene in our apparatus is between 5 K and 10 K.

4.2 Vibrational Cooling

To determine the degree of vibrational cooling, the fraction of vibrationally excited molecules in the electronic ground state was measured. Under normal operating conditions hot bands are not seen. When the sensitivity of detection is increased by several orders of magnitude, structure is sometimes recognized on the red side of the electronic origin. Care has to be taken to distinguish hot bands from lines of fragmented clusters of the molecules under study^{9, 10}. The vibrational temperature was measured for diphenylamine laser-desorbed from activated carbon.

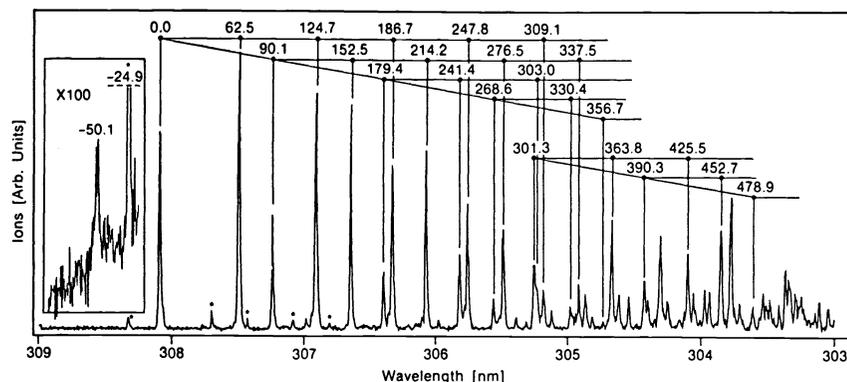


Figure 4: LD-JC/REMPI spectrum of diphenylamine.

Diphenylamine has low energy vibrational levels that are expected to be populated even at low temperatures. The spectrum is displayed in Figure 4. It was recorded by detecting the parent ions (169 amu), after resonant $S_1 \leftarrow S_0$ excitation followed by ionization at 355 nm. The laser fluence of the resonant excitation laser was about $1 \mu\text{J}/\text{mm}^2$. Several peaks indicated by an asterisk in the figure are due to diphenylamine-Ar complexes, most of which fall apart upon ionization and are detected on the diphenylamine mass. Long progressions of low-frequency vibrations are seen in the vibronic spectrum, thus transitions to these levels have good Franck-Condon overlap. It is expected, therefore, that hot bands, starting from vibrationally excited levels in the electronic ground state, have appreciable transition strength as well. In the inset the region on the red side of the electronic origin is shown 100 times enlarged, and a hot band is recognized, shifted by -50.1 cm^{-1} . This hot band is only observed when the delay of the detection lasers with respect to the desorption laser is such that an appreciable fraction of the molecules in interaction with the laser is warm (see Sect. 4.4). The 15 K vibrational temperature deduced from the relative intensity of the hot band with respect to the electronic origin is therefore an upper limit for the vibrational temperature. It should be noted that vibrational cooling is expected to be efficient for diphenylamine due to its low energy vibrations. In all molecules studied, however, the fraction of vibrationally excited molecules in the electronic ground state was less than 0.01.

5. BENZOIC ACID MONOMER SPECTRUM.

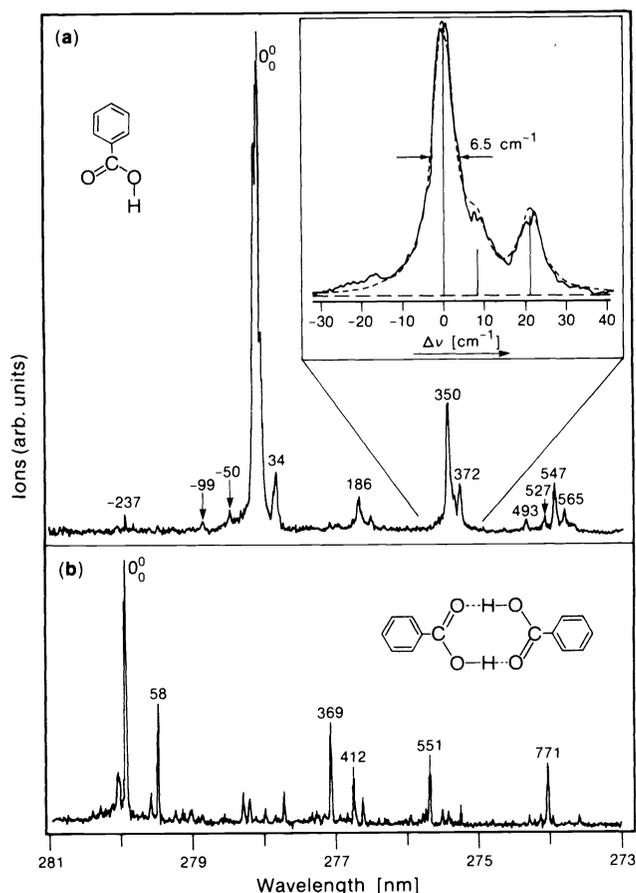


Figure 5: LD-JC/REMPI spectra of benzoic acid monomers (top) and dimers. Inset shows comparison with a simulated line profile.

Laser desorption can be used to obtain a "snapshot" of molecules on a surface. This idea can be illustrated by the measurement of benzoic acid monomers. Thermodynamical arguments predict that benzoic acid exists in the form of dimers at low temperatures¹⁸, and this is well documented experimentally by the work of Baum and McClure¹⁹⁻²². When benzoic acid is seeded in a beam using a heated nozzle, dimers are also expected to form in the expansion region. On the other hand, it is possible that the molecules exist on a surface as monomers, such that they can be laser desorbed in unclustered form. In general less clustering and dimer formation occurs when the molecules are entrained into the jet in the expansion region, compared to the approach in which the molecules are seeded in the beam. In fact, by laser desorbing this relatively volatile molecule from a suitable matrix an intense beam of benzoic acid monomers could be produced.

Benzoic Acid was dissolved in methanol and the solution was put into a $2 \times 4 \times 1 \text{ mm}^3$ piece of activated carbon. This material can contain a large amount of organics, and even benzoic acid, with a vapor pressure of approx. $5 \cdot 10^{-4}$ Torr at room-temperature, stays in this matrix for several days in 10^{-7} Torr vacuum. During the measurements, we desorbed from the same spot on the activated carbon for several hours at 10 Hz, without a significant decrease in signal.

The spectra we obtained are shown in Figure 5. The upper panel shows the spectrum of the benzoic acid monomer. All major resonances are due to the $S_1 \leftarrow S_0$ transition, induced by the dye laser, which is scanned from 281-273 nm.

Ions are detected at the parent mass (122 amu) after delayed ionization with the ArF laser out of the triplet state, which is populated via $S_1 \rightarrow T$ intersystem crossing. Above each peak in the spectrum the frequency distance to the electronic origin (in cm^{-1}) is indicated. The lower panel shows the spectrum of the benzoic acid dimer, also detected at the mass of the parent (244 amu). To observe this spectrum the dye laser used for the resonant excitation and the ArF laser used for ionization have to be overlapped in time; on the dimer mass no spectrum could be recorded for delay times longer than the fluorescence lifetime of the excited singlet state. The spectrum of the dimer is the same as that observed in LIF experiments^{23, 24}, and the mass-selection leaves no doubt over the origin of this spectrum.

The spectrum displayed in the upper panel of Figure 5 can be directly compared to the phosphorescence excitation spectrum shown by Kamei et al.²⁵. In both cases triplet state monomers are detected (with some delay), after resonantly exciting the species in the molecular beam. A comparison of both spectra shows that the monomer/dimer ratio in our beam is larger by about a factor of fifty compared to the monomer/dimer ratio in the experiment of Kamei et al. A more detailed interpretation of this spectrum is given elsewhere¹⁰.

6. BUCKMINSTER FULLERENE.

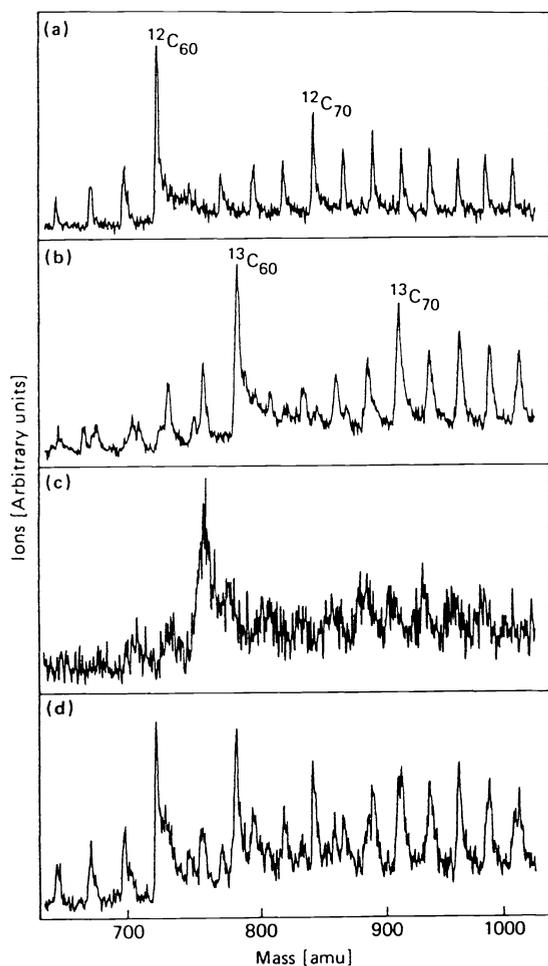


Figure 6: LD-JC mass spectra of carbon clusters formed by laser ablation of graphite in a separate step. See text for explanation of isotope scrambling.

An example of the analytical use of the ability to take a "snapshot" of what is on the surface is the detection of C_{60} molecules. These species had been conjectured in 1985 to have the icosahedral structure of soccerball, with the carbon atoms located on the vertices of 12 pentagons and 20 hexagons.²⁶ Recently this dramatic prediction has been confirmed experimentally, and quantities can now be made of these Buckey balls, so called after Buckminster Fuller²⁷. In one of the early attempts to do so, we laser vaporized graphite in an argon atmosphere, depositing the resulting soot on a copper surface. This surface, with its minute coverage of carbon products was subsequently analyzed in the LD-JC machine. A resulting spectrum with 193 nm non resonant ionization is shown in Figure 6.

It is extremely important to demonstrate that the observed spectra indeed reflect what is on the surface and that clusters are not formed in the desorption step. This can be shown with an isotope scrambling experiment as follows²⁸. Figure 6 (a) and (b) show the analysis of material formed by vaporizing pure ^{12}C and ^{13}C carbon respectively. Figure 6 (c) is the analysis of material formed by vaporizing a 50-50 mixture of the two isotopes. Finally, the bottom panel of Figure 6 is a LD-JC mass spectrum of material that was obtained by six sequential vaporizations of ^{12}C and ^{13}C powder onto the same surface. If the C_{60} would have been formed in the analysis step, then this last mass spectrum would have been similar to that in panel (c). Instead this last spectrum is similar to the sum of that in panels (a) and (b), showing that what is observed is in fact what is on the surface.

7. PARA-AMINO BENZOIC ACID (PABA).

Another example of the power LD-JC spectroscopy is the study of para-amino benzoic acid (PABA). The PABA molecule is of particular interest because it is closely related to both aniline and benzoic acid. Both these molecules are sufficiently volatile to be seeded in a beam^{25, 29, 30}. PABA, however, has a vapor pressure of 10^{-7} Torr at room-temperature³¹, and nothing has been known about its gas-phase spectroscopy until now, despite its widespread use as a sunscreen and as a photodegradation inhibitor.

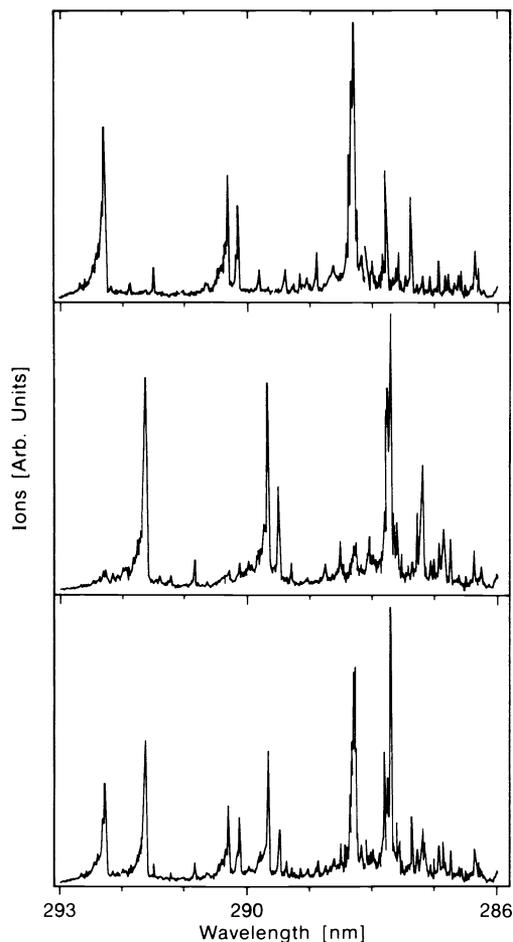


Figure 8: LD-JC/REMPI spectra of PABA dimers, with and without partial deuteration. Recorded at mass 274 (top), 278 (middle), and 276.

The next strong vibrations at 550.4, 812 and 995 cm^{-1} are ring vibrations as well. The lower energy vibrations involve motions of the substituent groups with respect to the ring. Since such low energy vibrations are absent in the aniline spectrum, they are most probably due to the COOH substituent.

Under slightly different desorption conditions, intense spectra could be recorded at mass 274, the mass of the PABA dimer. A typical dimer spectrum is shown in the top panel of Figure 8. This spectrum was recorded at mass 274, the mass of the unfragmented dimer. The dimer 0-0 band is blue-shifted by 42.0 ± 0.8 cm^{-1} with respect to that

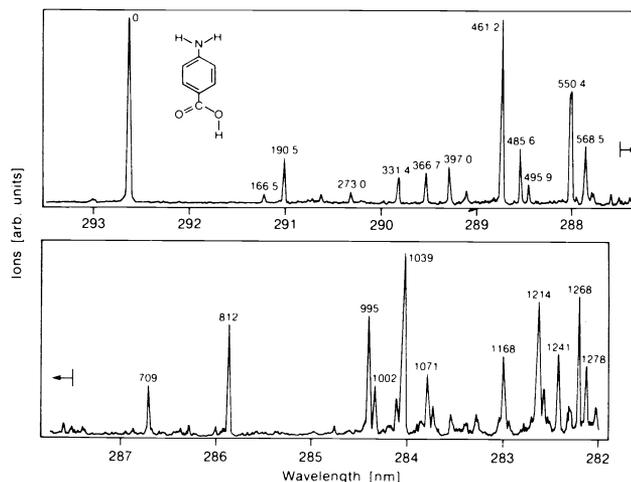


Figure 7: LD-JC/REMPI spectrum of para-amino benzoic acid.

The (1+1)-REMPI spectrum of the laser-desorbed, jet-cooled PABA is shown in Figure 7. The origin of the electronic transition is located at 292.63 nm (34173 ± 2 cm^{-1}). A large number of transitions to vibrational levels in the excited electronic state appear in the spectrum. The energy of each major peak in the spectrum of -- Figure id 'SPEC' unknown -- with respect to the electronic origin is indicated, in cm^{-1} , above each peak. Contrary to the observations in the methylbenzoate and the benzoic acid spectra²⁵, no sign of a rotational isomer of PABA is seen. Although a complete assignment of the vibrational spectrum of PABA does not yet exist, the first strong vibration at 461.2 cm^{-1} can be ascribed to the lowest-energy active ring vibration, corresponding to the 6a vibration in benzene.

of the monomer, as are most other lines. Spectra were recorded of PABA complexes consisting of different monomer units. For this, a mixed sample of PABA and PABA- d_2 (the two H-atoms in the ring ortho to the NH_2 group substituted by D-atoms; mass 139) was used. Substitution of one H-atom in the ring by a D-atom, gives a spectral blue-shift of about 38 cm^{-1} . In Figure 8 spectra obtained using a 1:1 mixture of PABA (mass 137) and PABA- d_2 (mass 139) are shown. The spectra of the three different kind of dimers, i.e. d_0-d_0 , d_2-d_0 and d_2-d_2 , were recorded in the same laser scan. The top spectrum shows the d_0-d_0 dimer spectrum, detected at mass 274. The middle spectrum is that of the d_2-d_2 dimer (mass 278) and all peaks show a shift with respect to the undeuterated dimer of $76 \pm 2\text{ cm}^{-1}$. The lower spectrum was recorded at mass 276 of the mixed d_2-d_0 dimer, and it is almost exactly equal to the sum of the first two spectra. From this it can be concluded that the excitation is localized in one of the monomer units; either one half or the other is excited in the loosely coupled dimer. One could say that by tuning the excitation wavelength we can choose in which ring the photon will be deposited. From a more detailed study of these spectra REF it is possible to calculate a small, positive value for the interaction energy, equal to $\epsilon = 0.4 \pm 0.3\text{ cm}^{-1}$, where the error is two times the standard deviation.

8. CONCLUSION

The above examples have been chosen to show the power of LD-JC both for organic surface analysis and for studying the spectroscopy of low vapor pressure and thermally labile complex organics. As demonstrated with perylene the method can be sensitive enough to detect as few as a million molecules in a 0.25 mm diameter spot. Rotational and vibrational cooling to below 10 K can be achieved, as demonstrated with Anthracene (rotation) and diphenylamine (vibration). Spectra can be recorded at the parent mass of the desorbed molecule. It is possible to use the laser desorption to obtain a picture of the molecules on the surface, as demonstrated with benzoic acid monomers and with Buckminster Fullerene. Finally, some of the capabilities for studying the spectroscopy of organic molecules are shown with the PABA molecule and its dimers.

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